Asian Journal of Chemistry Vol. 22, No. 3 (2010), 1661-1664

Low-valent Organometallic Derivatives of Palladium(O), Platinum(O) and Rhodium(I) with 4-Amino-5-mercapto-3-substituted-1,2,4-triazoles

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Low-valent organometallic derivatives of palladium(O) platinum(O) and rhodium(I) with 4-amino-5-mercapto-3-substituted-1,2,4-trizoles have been isolated from displacement reaction of $M(P\phi_3)_4$ (M = Pd/Pt) and $Rh(P\phi_3)_3Cl$ with methyl and ethyl substitution of ligand in benzene medium. Oxidation state of metals in these compounds are determined iodometrically. Most probable tetrahedral structure of Pd(O), Pt(O) and square planer configuration for Rh(I) have been assigned using various physico-chemical data. Metal ligand vibrations in the far-infrared spectra of complexes have been reasonably assigned.

Key Words: Palladium(O), Platinum(O), Rhodium(I), Complexes, Substituted-1,2,4-triazoles.

INTRODUCTION

Organometallic derivatives of platinum group metals are versatile homogeneous catalyst having unique and interesting insights into structure and bonding[1-3]. Wilkinson catalyst, $Rh(P\phi_3)_3Cl$ readily undergoes a variety of reactions, most of which involves either replacement of a phosphine ligand giving *trans*-products[4] or oxidation addition to form Rh(III) compounds[5] and also display adduct formation with a number of neutral donor molecules such as SO_2 and tetracyanoethylene[6] (TCNE). The abstraction of thiocarbonyl group from carbon disulphide to give *trans*-$(P\phi_3)_2$ Rh(CS)Cl have also been reported by Wilkinson *et al*[7]. Therefore, it is interesting to investigate reaction of $Rh(P\phi_3)_3Cl$ with 4-amino-5-mercapto-3-substi-tuted-1,2,4,-trizoles which display thione-thiol tautomerism[8] (Fig. 1), zerovalent $Pd(P\phi_3)_4$ and $Pt(P\phi_3)_4$ also dissociate and exhibits a spectacular reactivity in solution[3,9]. In view of these features, the present study reports displacement reactions and structural investigation of solid products isolated during reaction[10-12].

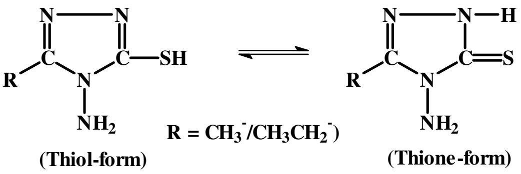

Fig. 1.

EXPERIMENTAL

All chemicals used were of A.R. or C.P. grade 4-amino-5-mercapto-3-alkyl-1,2,4-triazole[13], $[Pd(P\phi_3)_4]$[14], $[Pt(P\phi_3)_4]$[14] and $[Rh(P\phi_3)_3Cl]$[15] were prepared by the methods described in literature. All complexes were prepared using general method. A solution of $M(P\phi_3)_4$ (M = Pd or Pt) and $Rh(P\phi_3)_3Cl$ in dry benzene was mixed with ethanolic solution of the ligand in an appropriate molar ratio. The mixture was stirred for 2-3 h and then cooled in refrigerator. The complexes obtained with different metal ligand ratios, were washed with ice-cold benzene and dried in a vacuum desiccator over anhydrous $CaCl_2$. The physical and chemical data of organometallic derivatives is given in Table-1.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

S. no.	Compound	Colour	Analysis % found/(calcd.)			
			C	H	N	M
1	$[Pd(P\phi_3)_3(AMtTH)]$	Yellow	66.8 (66.9)	4.8 (4.9)	5.5 (5.4)	10.6 (10.4)
2	$[Pd(P\phi_3)_2(AMtTH)_2]$	Light yellow	51.2 (51.4)	4.9 (5.0)	12.3 (12.6)	12.1 (12.9)
3	$[Pd(P\phi_3)_2(AEtTH)_2]$	Deep yellow	57.6 (57.5)	4.9 (5.0)	12.3 (12.2)	11.8 (11.6)
4	$[Pt(P\phi_3)_2(AMtTH)_2]$	Golden yellow	51.6 (51.5)	4.2 (4.3)	11.6 (11.5)	20.0 (19.9)
5	$[Pt(P\phi_3)(AMtTH)_3]$	Yellow	52.3 (52.4)	3.6 (3.7)	11.3 (11.1)	19.4 (19.3)
6	$[Pt(P\phi_3)_2(AMtTH)(Py)]$	Yellow	70.7 (70.8)	6.1 (6.1)	10.6 (10.5)	29.1 (29.2)
7	$[Pt(P\phi_3)_2(AEtTH)_2]$	Deep yellow	52.5 (52.4)	4.6 (4.5)	11.1 (11.2)	19.8 (19.3)
8	$[Rh(P\phi_3)_2(AMtTH)Cl]$	Golden brown	59.2 (59.0)	4.5 (4.5)	7.2 (7.0)	13.0 (12.9)
9	$[Rh(P\phi_3)_2(AEtTH)Cl]$	Brown	60.0 (59.5)	4.6 (4.7)	7.0 (6.9)	12.9 (12.7)
10	$[Rh(P\phi_3)(AMtTH)_2Cl]$	Brown	43.7 (43.6)	4.1 (4.0)	17.1 (16.9)	15.7 (15.6)

IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer and electronic spectra on a Backmann DU-6 spectrophotometer. Molar conductance (10^{-3} M) of complexes were measured in DMF using Wiss-werkstatten Weihem obb type LBR conductivity meter. Magnetic measurements were made on a Gouy balance using $Hg[Co(SCN)_4]$ as calibrant.

RESULTS AND DISCUSSION

The methyl (AMtTH) and ethyl (AEtTH) derivatives of 4-amino-5-mercapto-3-substituted-1,2,4-triazole interacts with thione tautomeric form with $M(P\phi_3)_4$ (M = Pd or Pt) and $Rh(P\phi_3)Cl$ in benzene solution and replaces one molecule of $P\phi_3$ easily. Further replacement of $P\phi_3$ molecule occurs under more vigorous conditions by increasing the time of stirring. However, all $P\phi_3$ molecules could not be replaced by these thioamide ligands. When substitution reaction is carried out in benzene-pyridine mixture then mixed ligands complex $[Pt(P\phi_3)_2(AMtTH)Py]$ was resulted.

The stoichiometry of all solid products obtained after carring out substitution reaction is assigned on the basis of elemental analyses (Table-1). The molecular weight of complexes, as determined cryscopicaly indicate them to be monomeric and conductance measurement suggests them to be non-electrolyte. All solid compounds were found to be diamagnetic indicating d^{10}-configuration for Pd(O) and Pt(O) and d^8-configuration for Rh(I)[16]. When the suspension of these compounds were treated with iodine solution in CCl_4, the violet colour of iodine was discharged in all cases indicating the presence of Pd(O), Pt(O) and Rh(I) electronic state. However, determination of oxidation state of rhodium in the complexes were found by titration with ceric ammonium sulphate using ferrion as indicator following the method reported in literature[17]. The zerovalent state of palladium and platinum was also verified by iodometric and acidimetric titration[18]. It was found that 1 g mole of $[M(P\phi_3)_2(LH)_2]$ reacts with 2 g equiv. of iodine and the liberated 2 g mol of LH(ligand) consumes 2 g equiv. of NaOH suggesting zero oxidation state of palladium and platinum.

The electronic spectra of Rh(I) complexes display strong broad band between 25000-28000 cm^{-1} assigned to charge transfer band from filled metal $4d_z{}^2$ orbital to empty ligand π-orbital and square planar Rh(I) may be tentatively assismed[17,19,20]. However, other ligand field bands are obscured. All palladium(O) and platinum(O) complexes also exhibit CT band between 30,300-28,810 cm^{-1} and 30,000-29,420 cm^{-1}, respectively. The intensity of CT band is abnormally high and appears high degree of *d-p* mixing.

Infrared spectra: The ligand 4-amino-5-mercapto-3-substituted-1,2,4-triazole display three infrared bands at 3270, 3180 and 3100 cm^{-1} for methyl substitution (AmtTH) and at 3260, 3210 and 3110 cm^{-1} for ethyl substitution due to interaction between $-NH_2$ and -NH groups. These bands reamin almost unperturbed in position but higher intensity indicating the absence of bonding neither through amino nitrogen nor through iminonitrogen. Thioamide band I of ligand has mixed contributions from δ(N-H), δ(C-H) and ν(C-N) modes[21,22] observed at 1580 (AMtTH) and at 1570 (AEtTH) in ligands also remains uncharged in position on coordination to all Pd(O), Pt(O) and Rh(I) suggesting the absence of bonding through nitrgen atom.

The thioamide band (III) and (IV) observed at 1050 cm^{-1} and 925 cm^{-1} in ANtTH and at 1050 cm^{-1} and 770 cm^{-1} in AEtTH in the ligands have major contribution from $\nu(C \overset{\cdots}{-} S)$[23] on complexation thioamide band (III) is shifted lower frequency by about 60-65 cm^{-1} and band (IV) is also shifted by about 60-65 cm^{-1}. The logical consideration of these IR data suggests that the ligands AMtTH and AEtTH are coordinated through their sulphur atom and formation of strong metal sulphur band may be assumed[10].

The presence of coordinated pyridine[24] is indicated by broad band in the region of 3510-3400 cm^{-1} and medium to weak intensity bands at 670, 450 and 250 cm^{-1} in the spectrum of $[Pt(P\phi_3)_2(AMtTH)(Py)]$. In addition, bonds near 1515, 1505, 1450, 1070, 1040 and 695 cm^{-1} in the spectra of complexes suggests the presence of coordinated $P\phi_3$ molecule[25].

For IR spectra of complexes contains some new bands. One ν(Rh-P) band in $[Rh(P\phi_3)_2(AMtTH)Cl]$ and $[Rh(P\phi_3)_2(AEtTH)Cl]$ at 375 and 380 cm^{-1}, respectively suggests two $P\phi_3$ molecules are at *trans*-position in square planer structure. However, only one ν(Rh-P) (360 cm^{-1}), two ν(Rh-S) (320 and 300 cm^{-1}) and one ν(Rh-Cl)

(330 cm^{-1}) are present in [Rh(Pϕ_3)(AMtTH)$_2$Cl] probably due to incoming AMtTH ligand takes up *cis*-position and chloride ligand moves out of plane in the square planar structure. The lower position of ν(Rh-Cl) may be due to strong *trans*-influence of AMtTH.

Two ν(Pt-S) (330 and 320 cm^{-1}) an one ν(Pt-P) (460 cm^{-1}) in [Pt(Pϕ_3)(AMtTH)$_3$], two ν(Pd-P) 450-400 cm^{-1}) and one ν(Pd-S) (310 cm^{-1}) bands in [Pd(Pϕ_3)$_3$(AMtTH)] suggest C$_3$v- point group in Td-str. But two ν(Pt-P) 410 and 390 cm^{-1}) and two ν(Pt-S) (320 and 310 cm^{-1}) bands in [Pt(Pϕ_3)$_2$(AMtTH)$_2$] probably due to lower symmetry in Td. Str. Since. Pϕ_3 molecule exhibits several bands in far-IR region[26], so mixing of Pϕ_3 vibrations may not be reuled out.

Thus, on the basis of various physico-chemical data tertrahedral configuration for Pd(O) and Pt(O) and square planar structure for Rh(I) complexes may be reasonably assigned having bonding through thiocarbonyl sulphur in all.

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(*Received*: 14 February 2008; *Accepted*: 10 November 2009) AJC-8038